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(54) Title: PROCESS FOR REGENERATION OF ION-EXCHANGE RESINS USED FOR SUGAR DECOLORIZATION

(57) Abstract

Process for regeneration of ion-exchange resins, used in sugar decolorization, using a sucrose solution with sodium or calcium chloride, or another chloride, namely potassium or a mixture of those chlorides, alkalinised with calcium hydroxide. The effluent from this resin regeneration process, containing sucrose and a low content of chloride ions, can be used, directly or after a chemical or physical treatment, in sugar production or sugar refining processes.

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PROCESS FOR REGENERATION OF ION-EXCHANGE RESINS USED FOR SUGAR DECOLORIZATION.

"Process for regeneration of ion-exchange resins used for sugar decolorization, using chloride salts in a sucrose solution alkalinised with calcium hydroxide"

Technical field

The present invention refers to a regeneration process of ion-exchange resins used in the decolorization of sugar solutions in cane or beet sugar factories, sugar refineries, or in industries using sugar.

Background art

In the classic process for regeneration sugar decolorization resins, a solution of 10% of sodium chloride alkalinised with sodium hydroxide is used. However, this process of regeneration is not efficient in colorants removal from resin and produces polluted effluents. In fact, salt effluents resulting from resins regeneration by alkalinised solutions of sodium chloride are a big problem of pollution because they have a high content of organic compounds with a high content of sodium chloride.

Disclosure of the invention

In the innovator process that is presented here, the resin regeneration is done with a sucrose solution alkalinised with calcium hydroxide, containing a small quantity of calcium chloride or sodium chloride, or another chloride, for example, potassium chloride or a mixture of those chlorides.

The advantage of this process is that the solution

resulting from the regeneration, containing sucrose, can be used in sugar production or sugar refining, without causing pollution problems, as happens in the classic process of resin regeneration.

This new process takes advantage of the following points:.

- solubility of calcium hydroxide increases with sucrose concentration in solution;
- concentration of regenerating agents in this new process is much lower as compared with the classic sodium chloride regeneration;
- at this low salts concentration resin do not shrink as much as in the classic sodium chloride regeneration;
- calcium ions can be removed from effluent solutions by reaction with carbon dioxide, sodium carbonate, phosphoric acid, or sodium phosphate;
- sucrose solutions with calcium hydroxide resulting from this new regeneration process can be used as a neutralising agent for low purity products of sugar production or sugar refining.

Considering these facts, and in base of the present process we verify that we can regenerate resins, this is, remove the majority of the colorants fixed to the resin after the decolorization step; using a sucrose solution with calcium hydroxide and a small quantity of chloride ions.

In this new process, we use a sucrose solution containing 100 to 600g of sucrose per liter of solution, alkalinised with calcium hydroxide, containing 5 to 40g of CaO per liter of solution, and having calcium chloride or sodium chloride, or another chloride, as for example, potassium chloride or a mixture of those chlorides, in such a quantity that chloride ion concentration is between 3 to

30g per liter of solution.

The sucrose solution, resulting from this new regeneration process, containing calcium hydroxide, chloride salts and colorants removed from the resin, can be returned to the sugar production or sugar refining processes, directly, or after treatment with chemicals or through tangential filtration.

In fact, this solution can be treated with carbon dioxide, sodium carbonate, phosphoric acid or sodium phosphate, to remove calcium before be used in sugar production or sugar refining.

Also tangential filtration processes can be used to separate the salts of this solution before it be re-used in sugar production or sugar refining processes.

Ion-exchange resin to be regenerated using the regeneration process described in this patent must be contained in an appropriate column or columns for sugar decolorization process.

During the decolorization step, sugar solutions are fed to the resin column in an up-flow or down-flow way depending on the equipment used.

After the decolorization step, sugar solution inside the column is dislocated with water. During this procedure sucrose concentration in the column effluent decreases. When sucrose concentration reaches a value identical to sucrose in the regenerating solution, resin regeneration starts. For resin regeneration, a sucrose solution containing calcium hydroxide and sodium or calcium chloride or other chlorides, are fed to the resin column in a flow between 1 to 3 cubic meters per cubic meter of resin per hour and at a temperature between 40° to 70°C. The quantity of regenerating solution used in

this regeneration is between 2 to 4 cubic meters per cubic meter of resin inside the column.

After the passage through the resin of this regenerating solution, the resin is washed with water, decompressed with air and washed again as it is usual in the resin regeneration processes.

From time to time and as is usual in decolorization resins, an acid regeneration (NaCl + HCl) and alkaline regeneration (NaCl + NaOH) can be performed.

Prefered embodiment of the invention

This new resin regeneration process was experimentally used to regenerate a styrenic divinyl-benzenic resin with ammonium quaternay, initially in the chloride form. The resin, placed in a one liter column was used to decolorize carbonated liquor from a sugar refinery. After 40 BV (bed volumes) of liquor, the resin was washed and regenerated with this new resin regeneration process. In ten successive liquor cycles and regenerations, resin efficiency was maintained at a high level with decolorization of liquor higher than 90%.

In this experiment, the solution effluent from the resin regeneration, with this new process, was treated by Nanofiltration. It was observed that more than 90% of colour, measured at 420 nm at pH 7.0, was separated to the retentate. The permeate was used to prepare the regenerating solution, after adding the appropriate quantities of sucrose, calcium hydroxide and calcium chloride. Resin regenerated with this permeate maintained the efficiency above 90% of decolorization.

Claims

1 - Process for regeneration of sugar decolorization ion-exchange resins, characterised by using a sucrose solution containing calcium, sodium or potassium chloride, or a mixture of these compounds, alkalinised with calcium hydroxide.

2 - Process for regeneration of sugar decolorization ion-exchange resins according to claim 1, characterised by the resin regeneration being performed at a flow between 1 to 3 cubic meters of regenerating solution per cubic meter of resin, per hour, at a temperature between 40° to 70°C.

3 - Process for regeneration of sugar decolorization ion-exchange resins according to claims 1 and 2, characterised by the regeneration being performed with a sugar solution containing 100 to 600g of sucrose per liter of solution and calcium hydroxide in a quantity between 5 to 40g of CaO per liter of solution and calcium chloride, sodium chloride, or potassium chloride or a mixture of these compounds in such a quantity that chloride ion concentration will be between 3 to 30g of chloride per liter of solution. This regenerating solution is passed through the resin in a quantity between 2 to 4 cubic meters per cubic meter of resin.

4 - Process for regeneration of sugar decolorization ion-exchange resins according to claims 1, 2 and 3, characterised by the effluent resulting from this regeneration process being used in the sugar production or sugar refining processes, directly or after a previous treatment.

5 - Process for regeneration of sugar decolorization ion-exchange resins according to claim 4, characterised by the fact that one possibility of treatment of the effluent resulting from this regeneration process consists in the calcium precipitation with carbon dioxide, sodium carbonate, phosphoric acid or sodium phosphate.

6 - Process for regeneration of sugar decolorization ion-exchange resins according to claim 4, characterised by the fact that colorants in the effluent from the regeneration can be separated by tangential filtration, resulting a retentate with the majority of colorants, to be used in the sugar production or sugar refining processes, and a permeate that can be used to prepare the regeneration solution.

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Interna al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C13D3/14 B01J49/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C13D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 032 263 (AKZO) 22 July 1981 see page 3, line 6 - page 5, line 6 see page 20-22; examples 14,15 ---	1-5
A	EP,A,0 369 831 (REFINARIAS DE ACUCAR REUNIDAS) 23 May 1990 see column 4-5; claims 1-9 ---	1,5
A	CHEMICAL ABSTRACTS, vol. 104, no. 6, 10 February 1986 Columbus, Ohio, US; abstract no. 35880e, OIKAWA SHOZO 'NEW REGENERATION SYSTEM FOR SOFTENER RESIN IN BEET SUGAR FACTORY' page 108; column 2; & SEITO GIJUTSU KENKYU KAISHI 1984,(33), 43-8 (Jp) see abstract --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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A	DATABASE WPI Week 9311 Derwent Publications Ltd., London, GB; AN 93-091694 & SU,A,1 723 135 (KURSK SECT SUGAR IND RES) , 30 March 1992 see abstract	1
A	EP,A,0 016 992 (ASSALINI) 15 October 1980	
A	FR,A,1 404 591 (MAGYAR CUKORIPAR KUTATO INTEZETE) 24 May 1965	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interna al Application No
PCT/PT 95/00006

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-32263	22-07-81	NL-A-	7909337	16-07-81
		AT-T-	11112	15-01-85
		BG-A-	49501	15-11-91
		CA-A-	1150249	19-07-83
		JP-C-	1403054	28-09-87
		JP-A-	56097540	06-08-81
		JP-B-	62011615	13-03-87
		SU-A-	1228779	30-04-86
		US-A-	4353992	12-10-82
EP-A-369831	23-05-90	AT-T-	117915	15-02-95
		CA-A-	2007487	10-07-91
		DE-D-	68920959	16-03-95
		DE-T-	68920959	12-10-95
EP-A-16992	15-10-80	NONE		
FR-A-1404591	10-11-65	NONE		